

RATE CONSTANT FOR REACTION OF ATOMIC HYDROGEN WITH GERMANE

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Due to the interest in the chemistry of germane in the atmospheres of Jupiter and Saturn, and because previously reported kinetic reaction rate studies at 298 K gave results differing by a factor of 200, we performed laboratory measurements to determine the reaction rate constant for $\text{H} + \text{GeH}_4$. Results of our study at 298 K, obtained via the direct technique of flash photolysis-resonance fluorescence, yield the reaction rate constant, $k = (4.08 \pm 0.22) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$.

INTRODUCTION

The possibility of detecting germane (GeH_4) in the reducing atmosphere of Jupiter by means of high resolution infra-red absorption spectroscopy was suggested by Corice and Fox¹ in 1972. Germane was subsequently identified as present in Jupiter's atmosphere by Fink et al.² It has also been recently reported by Noll et al.³ as observed in the atmosphere of Saturn. Of particular note is the conclusion that GeH_4 is not the major reservoir of the total expected germanium in either planet. Thus studies of germanium-containing molecules to determine their photochemistry and reactions which may either produce or remove GeH_4 are of interest. One of these reactions to consider is that of $\text{H} + \text{GeH}_4$. Based on a correlation of activation energy vs. bond length for a series of H-atom abstraction reactions, a 298 K value of $1.3 \times 10^{-11} \text{ cm}^3 \text{ s}^{-1}$ is predicted for the rate constant of this reaction. Previously reported studies^{4,5} yielded results at 298 K of $2 \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$ and $4 \times 10^{-10} \text{ cm}^3 \text{ s}^{-1}$, values differing by a factor of 200. Due to the interest in germanium chemistry in the atmospheres of the giant planets, and because of this discrepancy in the kinetic data, we have initiated a study to measure the reaction rate constant for $\text{H} + \text{GeH}_4$.

EXPERIMENTAL

The present kinetic experiments were performed by the direct technique of flash photolysis production of hydrogen atoms coupled with time-resolved resonance fluorescence detection and measurement of H-atom decay signal due to reaction with GeH_4 . A schematic diagram of the apparatus is shown in Figure 1. Previous publications from this laboratory have described in detail the apparatus and experimental procedures employed as well as applications to atmospheric hydrogen atom reaction studies.⁶⁻⁸

Briefly, in the present study, flash photolysis of germane and methane highly diluted in argon was the source for production of atomic hydrogen. Methane was chosen as an additional H-atom source in most experiments to obtain sufficient initial signal intensity beyond that produced from the relatively low germane concentrations. In this study, the $[\text{CH}_4]$ ranged from 0 to $8.91 \times 10^{15} \text{ cm}^{-3}$. The $[\text{GeH}_4]$ was $\sim 10^{13} \text{ cm}^{-3}$ which is $\gg [\text{H}] \ll 10^{11} \text{ atoms cm}^{-3}$. Thus, pseudo first-order conditions were achieved and the decay of H-atoms is represented by the equation:

$$\ln[\text{H}] = -k_{\text{observed}}t + \ln[\text{H}]_0.$$

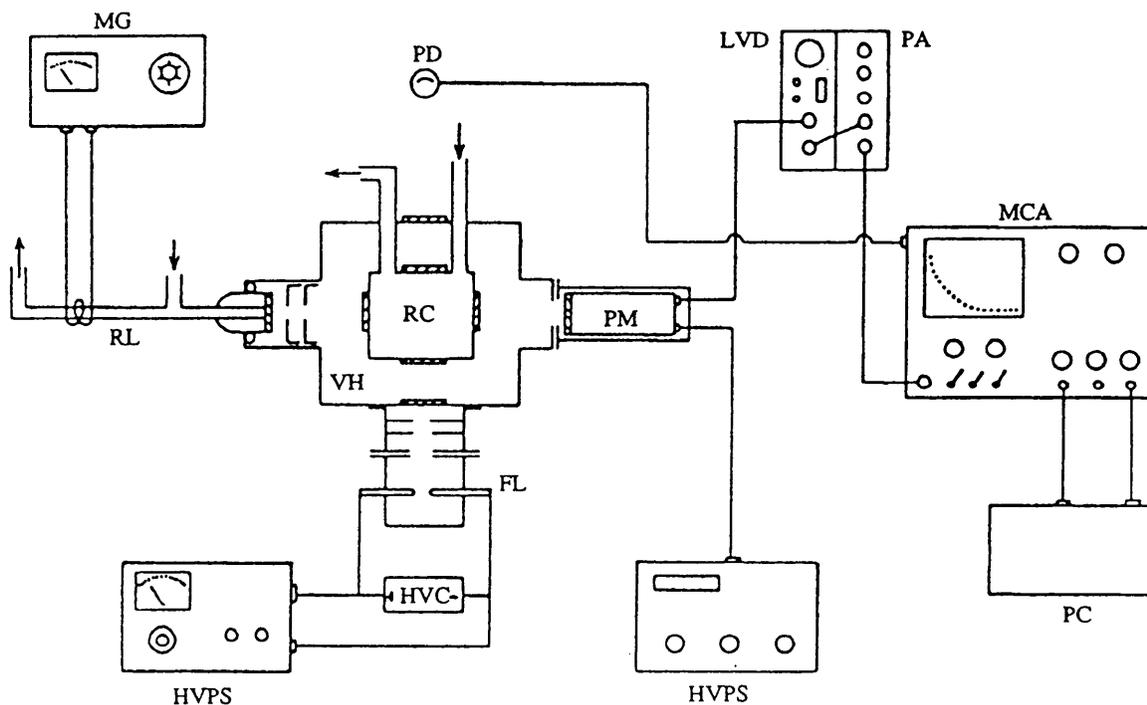
The observed pseudo first-order decay constant is given by:

$$k_{\text{observed}} = k_1[\text{GeH}_4] + k_d$$

where k_1 is the effective bimolecular rate constant and k_d (measured under identical conditions as for the reaction experiments, except in the absence of GeH_4) is the first-order rate constant for diffusional loss of H-atoms from the reaction zone viewed by the photon detector.

RESULTS

Since $[\text{H}]$ is proportional to fluorescent counts, k_{observed} and k_d were determined from linear least-squares analysis of plots of the logarithm of accumulated fluorescent counts vs. time. The linearity of such plots, as illustrated in Figure 2, demonstrates that the measurements are representative of a first-order process. Experiments to determine the



FLASH PHOTOLYSIS-RESONANCE FLUORESCENCE SYSTEM:
 MG = MICROWAVE GENERATOR RL = RESONANCE LAMP RC = REACTION CELL
 VH = EVACUATED OUTER CHAMBER FL = FLASH LAMP PM = PHOTOMULTIPLIER
 PC = PERSONAL COMPUTER HVPS = HIGH VOLTAGE POWER SUPPLY PD = PHOTODIODE
 HVC = HIGH VOLTAGE CAPACITOR LVD = LOW VOLTAGE DISCRIMINATOR
 MCA = MULTICHANNEL ANALYZER PA = POWER AMPLIFIER
 (RL, FL, AND PM are at right angles to each other)

Figure 1. SCHEMATIC OF THE FLASH PHOTOLYSIS-RESONANCE FLUORESCENCE APPARATUS

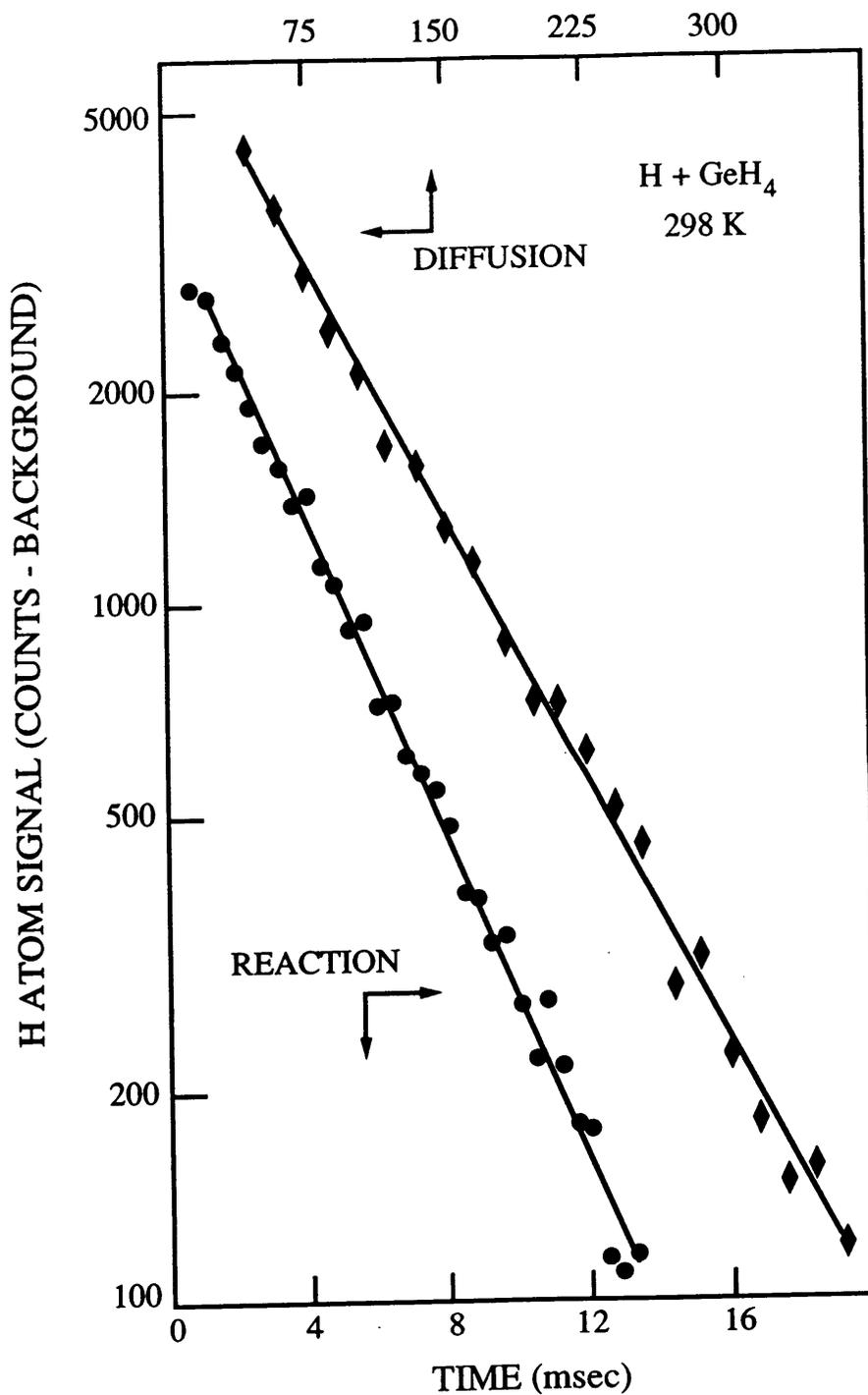


Figure 2. Examples of first-order decay plots of H atom diffusion and reaction at 298 K. The lines are determined from linear least-squares analysis of the data points.

reaction rate constant for $\text{H} + \text{GeH}_4$ were more difficult to perform than usual because, in most cases, the measured k_{observed} values exhibit a positive dependence upon flash intensity. A modified experimental procedure was therefore necessary. Sets of experiments were performed as a function of flash intensity; each set at a fixed total pressure of reaction mixture (i.e., constant concentration of GeH_4). The intercept from the linear least-squares analysis of each pressure set plot of $(k_{\text{observed}} - k_d)$ vs. flash energy yielded the resultant $(k_{\text{observed}} - k_d)$ for the respective total pressure set of experiments. The minimum measured $(k_{\text{observed}} - k_d)$ value (i.e., at the lowest flash energy) generally was not significantly different from the zero flash energy intercept. Results from the experiments are summarized in Table 1. The bimolecular reaction rate constant for $\text{H} + \text{GeH}_4$ was then obtained from the slope of the linear least-squares fit of this $(k_{\text{observed}} - k_d)$ data plotted in Figure 3 vs. $[\text{GeH}_4]$.

DISCUSSION

Results of our study of $\text{H} + \text{GeH}_4$ at 298 K yield the reaction rate constant, $k = (4.08 \pm 0.22) \times 10^{-12} \text{ cm}^3 \text{ s}^{-1}$. The difficult nature of interpreting the kinetic behavior of this reaction may have led to the higher rate constant value previously reported by Choo et al.⁵ The moderate reaction rate constant, which we obtained by our direct technique, is in reasonable agreement with the relative value reported by Austin and Lampe⁴ and is within a factor of ~ 3 of that predicted from a correlation of activation energy vs. H-atom bond length. This moderate reaction rate constant warrants additional laboratory interest for its potential relevance regarding the atmospheres of Jupiter and Saturn. We are initiating a temperature dependence study in order to provide kinetic data more appropriate to the atmospheric temperatures of the giant planets.

Acknowledgment

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Table 1: REACTION RATE DATA FOR H + GeH₄ AT 298 K

| P _{TOTAL} (Torr) | [GeH ₄] (10 ¹³ cm ⁻³) | FLASH ENERGY (J) | # of DECAYS | k _{obs} - k _d (s ⁻¹) |
|------------------------------|-------------------------------------------------------------|------------------------|----------------|---------------------------------------------------------|
| 25 | 0.837 | 20 - 352 | 7 | 52.0 |
| 25 | 0.837 | 81 - 352 | 4 | 55.0 |
| 55 | 1.59 | 36 - 225 | 6 | 77.5 |
| 25 | 1.72 | 36 - 225 | 3 | 131 |
| 50 | 2.48 | 36 - 324 | 4 | 154 |
| 25 | 2.65 | 20 - 182 | 4 | 148 |
| 110 | 3.18 | 36 - 225 | 6 | 138 |
| 100 | 3.35 | 20 - 352 | 7 | 144 |
| 100 | 3.35 | 36 - 352 | 6 | 171 |
| 50 | 3.43 | 56, 81 | 2 | 149 |
| 50 | 4.19 | 20 - 182 | 4 | 202 |
| 75 | 5.15 | 56, 81 | 2 | 242 |
| 75 | 6.28 | 20 - 182 | 4 | 277 |
| 100 | 6.86 | 56, 81 | 2 | 325 |
| 150 | 7.44 | 36 - 81 | 3 | 323 |

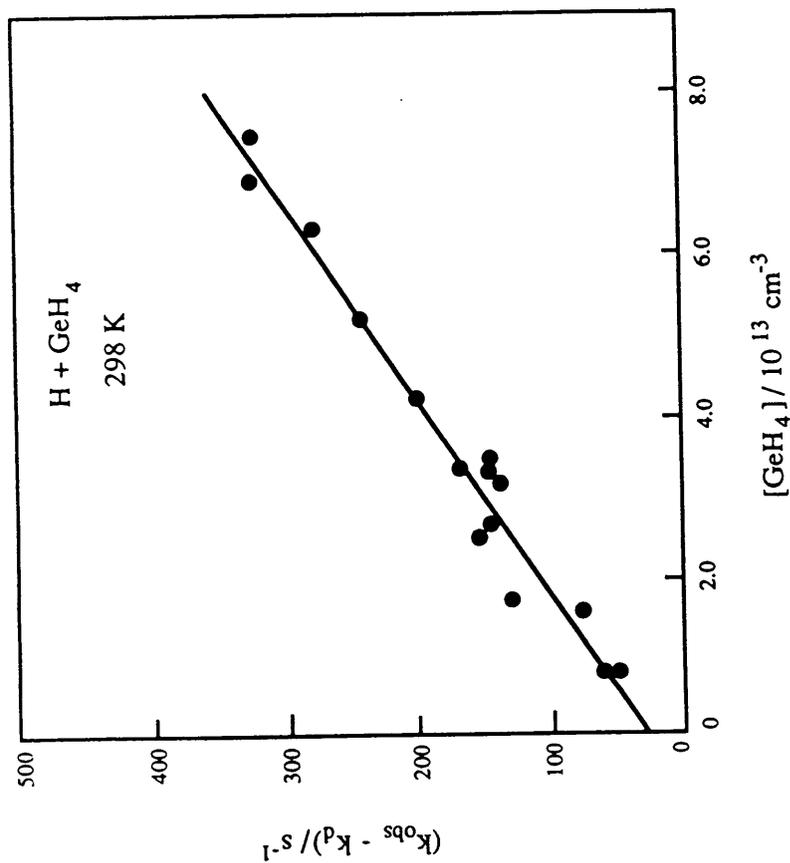


Figure 3. First-order decay constants vs. germane concentrations. The line is the linear least-squares fit of these data. The slope of this line is the reaction rate constant, k , for H + GeH₄ at 298 K.

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